# Novel Electrostatic Digital Printing Device Based on Single Walled Carbon Nanotube Film

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# ABSTRACT

Carbon nanotube thin films because of their unique optical and electronic properties coupled with the flexibility and easy patternability are promising candidates for application in low cost, large area flexible displays and optoelectronics. In this work, a novel printing device comprising a single-walled carbon nanotube (SWCNT) thin film and a molecularly doped polymer layer of arylamine in polycarbonate is reported. Results show that hole injection from the SWCNT thin film to the arylamine layer occurs under the influence of an electric field. The efficiency of the hole injection process was found to be dependent of the surface conductivity of the SWCNT film and the strength of the electric field across the bilayer device. The use of this hole injection process to generate electrostatic latent images for novel digital printing application is discussed.

*Keywords*: carbon nanotube films, printing device, electrostatic latent image, electron transfer, hole injection

#### **1 INTRODUCTION**

The basic steps in the xerographic (electrophotographic) process involve charge and imagewise discharge of the photoconductor to create the electrostatic latent image, followed by development of the latent image with toner electrostatically and then image fixation with heat and pressure [1]. Xerography has become a multi-billion dollar industry and the technology is applying to almost all color laser printers ranging from low speed printers in home office to high speed color presses in print shop. It is interesting to note that, other than the image file input through the laser ROS, which is digital, the entire printing process is still in an analog mode. In this work, we report a study of a new electron transfer reaction from a molecularly doped layer of an arvl amine in polycarbonate to a thin film of single walled carbon nanotube. The net result of this electron transfer reaction is a hole injection from the CNT film to the arylamine charge transport layer. This hole injection process triggers the discharge of the bilayer device process. In addition, this hole injection process is shown to be sensitive to the applied electric field as well as the conductivity of the CNT film. The mechanism for the charge-discharge process of the bilayer is proposed. The use of the bilayer device to digitize the xerographic printing process is discussed.

#### **2 EXPERIMENTAL**

*Materials*. Single walled carbon nanotube films of surface resistivity ranging from ~ 100 ohms/sq to ~ 5000 ohms/sq) on Mylar substrate were prepared using the procedure as described by Weeks et. al. [2]. Hole transporting molecule, TPD [3] and the polycarbonate polymer binder PCZ200 were obtained from internal source (structures in Fig. 1). All coating solvents (methylene chloride, tetrahyfrofuran and toluene) were analyzed reagent grade from Fischer and were used as received.

Devices. The bilayer devices studied in this work was fabricated by simply coating a solution containing TPD and PCZ200 in a mixed solvent of tetrahydrofuran and toluene (70:30 in ratio) over the carbon nanotube film (on Mylar) on a lab draw-down coater using a 5 mil draw bar. A typical coating solution consisted of ~ 14% of solid. The concentration of TPD in the charge transport layer (CTL) was at 40% by wt. The thickness of the CTL was typically ~ 20  $\mu$ m and was controlled by the solid concentration of the coating solution as well as the wet gap of the draw bar. The resulting bilayer device was air dried for 0.5 hour followed by vacuum drying at 100°C for 2 hours before electrical evaluation.

*Measurements and Techniques.* The surface resistivity of the carbon nanotube films were measured by a four probe point method using a Keithley 237 high voltage source measure unit. The charge-discharge characteristics of the bilayer device were performed on an in-house static scanner. Gold dot was evaporated on the CTL for the electrical contact. A schematic description of the apparatus is shown in Figure 1. Typically the bilayer devices were charged by the HV corona device and the surface potential were monitored using an electrostatic voltmeter (ESV). Since the bilayer device was "static" throughout the measurement, the charging and monitoring of the surface potential was controlled electronically through the electric circuit within the static scanner, typically there was a  $\sim 0.1$  s delay between charging and monitoring.



Fig. 1 A schematic of the "static" scanner.

#### **3 RESULTS AND DISCUSSION**

# **3.1 Device Configuration and Electrical Characterization**



Fig. 2 Bilayer device: configuration and materials used.

Figure 2 shows the configuration of the bilayer device and the materials used in this work. The device comprises a molecularly doped charge transport layer (CTL) made of hole transport molecule TPD in polycarbonate [3] over a thin film of pure single walled carbon nanotube on a Mylar substrate. The charge and discharge characteristic of the bilayer device was studied on an in-house static scanner (Fig. 1). Figure 3a shows the surface potential curves obtained from a typical CNT bilayer device. Figure 3b shows the surface potential curves from a controlled bilayer device where the CNT film is replaced by a Ti/Zr metal layer. By comparing with the control, the result indicates that the CNT bilayer device is charge capacitively. Unlike the control, the CNT bilayer device undergoes rapid discharge as soon as the electric field across the bilaver device is established.

Based on the results in Figure 3, the discharge of the CNT bilayer device can be schematically summarized in Figure 4. As soon as the bilayer is charged up and an electrical field is established, the field facilitates an electron-transfer reaction from TPD to the CNT film (or hole injection in the opposite direction). This is followed by a series of isoenergetic electron-transfer across the CTL, leading to nearly total discharge of the bilayer device [3].



Fig. 3 (a) Typical charge – discharge curves for a CNT bilayer device, and (b) charge – discharge curves for a controlled bilayer device.



Fig. 4 Schematic illustration of the charge – discharge process.

## **3.2 Effect of Surface Resistivity of Carbon** Nanotube Films on Discharge Rate

The rate of the dark discharge was found to be sensitive to the conductivity of the CNT film for a common CTL (40% TDP in polycarbonate, ~ 18  $\mu$ m thick). Figures 5a and 5b depict the discharge curves for two bilayer devices with CNT films of different surface resistivity. The result shows that the higher the conductivity of the CNT film, the faster the discharge rate and the more sensitive the device is.



Fig. 5 Charge – discharge curves for bilayer devices with CNT films of different surface resistivity (a) 250 Ohm/Sq and (b) 5000 Ohm/Sq.

## 3.3 Effect of Electric Field on Discharge Rate

From the discharge curves in Figures 5a and 5b as well as similar plots obtained from bilayer devices of different CNT surface resistivity, one can analyze the initial discharge rates at different surface potential for these devices. Plots of the initial discharge rate (dV/dt) of these bilayer devices at different surface potentials are given in Figure 6.



Fig. 6 Plot of initial discharge rate as a function of surface potential for bilayer devices with varying CNT surface resistivity.

The results indicate that (1) the discharge rate is highly sensitive to the surface resistivity of the CNT film, the higher the conductivity, the faster the discharge rate. (2) The discharge rate increases as the surface potential increases. Since the thickness of all these devices are held to be constant,  $\sim 18 \mu m$ , the result indicates that there is a strong electric field effect on the discharge rate, the higher the electric field across the device, the faster the discharge rate. Another important feature in Figure 6 is the apparent existence of a threshold electric field for the discharge rate. Specifically, dV/dt becomes negligible when the surface potential is < 200 V or when the electric field across the device is <  $\sim 10 V/\mu m$ .

The conclusions on the field and the threshold effects on dV/dt are substantiated by a second set of experiments where we vary the electrical field systematically by varying the CTL thickness.

#### 3.4 Proposed Discharge Mechanism

The results in Figures 5 and 6 clearly suggest that the discharge rate of the CNT bilayer device is very sensitive to the electric field. There also appears to be a threshold field to trigger the discharge process. We hypothesize that, under the influence of the electrical field, "bounded" electron-hole (e-h) pairs are generated in the bilayer device. At fields weaker than the threshold field, the e-h pairs recombine and no discharge occurs. On the other hand, when the field across the bilaver device is higher than the threshold field, the e-h pairs dissociate. This is followed by an electron transfer from the arylamine CTL to the CNT film. In other words, hole injection from the CNT film to the CTL results. The injected holes then migrate across the CTL, discharging the bilayer device. This hypothesis is supported by the observation that the discharge process is facilitated when the conductivity of the CNT film is high. Presumably, the bounded e-h pair can also dissociate under weak field when the CNT film is conductive. The mechanistic picture of the e-h pair generation and dissociation is summarized in Figure 7.



Fig. 7 Proposed discharge mechanism for the CNT bilayer device.

#### **4 CONCLUDING REMARKS**

In this work, we report a new electric field induced electron transfer reaction between an arylamine hole transport molecule, TPD, and single walled carbon nanotube thin film in bilayer device. Evidence is provided that bounded e-h pairs are formed under the influence of an electric field. At field strength lower than the threshold field, the e-h pairs recombine harmlessly. At higher electric fields, the e-h pairs dissociate, and this is followed by a hole injection reaction and a series of isoenergetic electron transfer across the CTL, leading to total discharge of the bilayer device. In separate experiments, we demonstrate that we can successfully develop the latent electrostatic images from the bilayer device with toner electrostatically. Since CNT films are known to be patternable, we suggest that, we should be able to digitize the xerographic process when we couple the discharge process of the present bilayer device with an addressable TFT backplane.

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#### REFERENCES

 For reviews about materials and the xerographic process, please see, D. Weiss and M. A. Abkowitz, Chem. Rev., 110, 479, 2010; also K. Y. Law, Chem. Rev., 93, 449, 1993.
C. Weeks, P. Glatkowski and D. Britz, MicroNano, 12, 1,

2007.

[3] D. M. Pai, J. F. Yanus and M. Stolka, J. Phys. Chem., 88, 4714, 1984.